

PTO 07-6996

CC=JP  
DATE=20030603  
KIND=A  
PN=15160330

METHOD FOR MANUFACTURING ALUMINA HOLLOW PARTICLES  
[Arumina Chuku Ryushi No Seizo Hoho]

Takayuki Kato et al.

UNITED STATES PATENT AND TRADEMARK OFFICE  
WASHINGTON, D.C. SEPTEMBER 2007  
TRANSLATED BY Schreiber Translations, Inc.

PUBLICATION COUNTRY	(10) :	Japan
DOCUMENT NUMBER	(11) :	15160330
DOCUMENT KIND	(12) :	A
PUBLICATION DATE	(43) :	20030603
APPLICATION NUMBER	(21) :	02012069
APPLICATION DATE	(22) :	20020121
INTERNATIONAL CLASSIFICATION	(51) :	C 01 F 7/02
PRIORITY COUNTRY	(33) :	JP
PRIORITY NUMBER	(31) :	01278203
PRIORITY DATE	(32) :	20010913
INVENTOR(S)	(72) :	Takayuki Kato et al.
APPLICANT(S)	(71) :	Yazaki Corporation
DESIGNATED CONTRACTING STATES	(81) :	
TITLE	(54) :	<b>METHOD FOR MANUFACTURING ALUMINA HOLLOW PARTICLES</b>
FOREIGN TITLE	[54A] :	<b>Arumina Chuku Ryushi No Seizo Hoho</b>

## Specification

### 1. Title of the invention

Method for Manufacturing Alumina Hollow Particles

### 2. Claims

1. A method for manufacturing alumina hollow particles, characterized by the fact that in a method for manufacturing alumina hollow particles with a hollow structure by forming a porous shell layer through binding of alumina powders, a resin powder and alumina powders with a diameter smaller than that of the resin powder are mixed while press-contacting; a precursor is formed being constituted by coating the surface of the resin powder in a state in which the alumina powders are partially embedded; the resin powder is burnt down by baking the precursor; and the alumina powders are sintered.

2. The method for manufacturing alumina hollow particles of Claim 1, characterized by the fact that a mixture of the alumina powders and silica powders with a

---

<sup>1</sup> Numbers in the margin indicate pagination in the foreign text.

diameter smaller than that of the alumina powders is press-contacted with the resin powder.

3. The method for manufacturing alumina hollow particles of Claim 2, characterized by the fact that in the mixture of the alumina powders and the silica powders, the silica powders are less than 50 wt%.

4. The method for manufacturing alumina hollow particles of any of Claims 1-3, characterized by the fact that as the resin powder, a polymethyl methacrylate powder classified at a particle diameter of 20  $\mu\text{m}$  or smaller is used.

5. The method for manufacturing alumina hollow particles of any of Claims 1-4, characterized by the fact that the precursor is treated at 700-800°C and sintered at an alumina sintering temperature.

### 3. Detailed explanation of the invention

[0001]

(Technical field of the invention)

The present invention pertains to a method for manufacturing alumina hollow particles with a hollow structure by forming a porous shell layer through binding of alumina powders. In particular, the present invention pertains to a method for obtaining alumina hollow particles

that have a binding strength of alumina powders and exhibits a true spherical shape.

[0002]

(Prior art)

For example, for the lightness of materials, the increase of the strength, etc., composite materials in which alumina particles were dispersed in a matrix such as metal are broadly used. Also, nowadays, for a further lightness, alumina hollow particles in which a porous shell layer with an approximate spherical shape is formed by binding alumina powders and the inside is made hollow are also used.

[0003] These alumina hollow particles are generally manufactured by forming a precursor in which the entire surface of a resin powder with a large diameter being a core material is coated with a powder layer composed of alumina powders with a diameter smaller than that of the resin powder, removing the resin powder from the precursor, and forming a porous shell layer in which the alumina powders are bound. For example, a method that forms a powder layer composed of alumina powders as a precursor on the entire surface of a polymer powder with high water absorptivity by contacting the polymer powder with high water absorptivity swollen by absorbing water and alumina

powders, removes the polymer with high water absorptivity by drying or baking the precursor at high temperature, and manufactures alumina hollow particles with a hollow structure is described in Japanese Kokai Patent Application No. Hei 10[1998]-258223.

[0004]

(Problems to be solved by the invention)

However, in the conventional manufacturing method, as schematically shown in Figure 8, since alumina powders 11 are only adhered to the surface of a resin powder 10, the alumina powders 11 are easily peeled off and dropped from the resin powder 10 at a time of high-temperature drying or baking, and the powder layer is difficult to be uniformly held. Furthermore, since the resin powder 10 is thermally expanded or evaporated by the high-temperature drying or baking, the alumina powders 11 are subjected to a pressure toward the outside, so that the powder layer is easily collapsed. As a result of the peeling-off of the alumina powders 11 and the collapse of the powder layer, a homogenous porous shell layer is not formed, and they become large obstacles to the increase of the productivity of the alumina hollow particles.

[0005] Also, nowadays, for a further advance of the lightness, the demand on fine alumina hollow particles with

a particle diameter of 20  $\mu\text{m}$  or smaller has also been raised, and for this reason, fine alumina powders with an order of submicron cannot but be used. However, it is further difficult to maintain a uniform powder layer of these fine alumina powders and to form a favorable porous shell layer.

[0006] The present invention considers this situation, and its purpose is to provide a manufacturing method suitable for fine alumina hollow particles with a particle diameter of 20  $\mu\text{m}$  or smaller in which the binding force of the alumina powders is strong, a homogeneous strong porous shell layer can be formed, the shape is near a true sphere, and especially, the increase of the demand will be anticipated.

[0007]

(Means to solve the problems)

In order to achieve the above-mentioned purpose, the present invention provides a method for manufacturing alumina hollow particles characterized by the fact that in a method for manufacturing alumina hollow particles with a hollow structure by forming a porous shell layer through binding of alumina powders, a resin powder and alumina powders with a diameter smaller than that of the resin powder are mixed while press-contacting; a precursor is

formed being constituted by coating the surface of the resin powder in a state in which the alumina powders are partially embedded; the resin powder is burnt down by baking the precursor; and the alumina powders are sintered.

[0008]

(Embodiment of the invention)

Next, a preferred embodiment of the present invention is explained in detail.

[0009] In the method for manufacturing alumina hollow particles of the present invention, first, a resin powder and alumina powder were pressed against each other, that is, mixed while press-contacting. With this press-contact mixture, as schematically shown in Figure 1, a precursor in which the surface of the resin powder 10 is coated in a state in which part of the alumina powders 1 are embedded is obtained. With the adoption of this coating state, the alumina powders 11 are not peeled off and dropped when they are baked thereafter, and the alumina powders are bound while favorably maintaining the coating state, so that a homogeneous strong porous shell layer composed of the alumina powders 11 can be formed.

/3

[0010] As an apparatus for applying the above-mentioned press-contact mixture, for example, an apparatus



schematically shown in Figure 2 can be mentioned. Said press-contact mixer 1 is approximately constituted by arranging an inner 3 and a scraper 4 at a prescribe distance at the central axis of a chamber 2 that is freely rotated and exhibits a drum shape. In the inner 3, the surface opposite to the inner wall of the chamber 3[sic; 2] exhibits an approximately semicircular sectional shape so that a mixed powder 5 can be smoothly introduced and fed out, and a slight gap is formed between the inner and the inner wall of the chamber 2. Also, as the press-contact mixture 1 with this constitution, for example, a mechanofusion system (AM-15F made by Hosokawa Micron K.K.) is known.

[0011] In the press-contact mixture, first, the mixed powder 5 of the resin powder 10 and the alumina powders 11 is charged into the chamber 2, and the chamber 2 is rotated at high speed in an arrow direction. Along with this rotation, the mixed powder 5 is pressed against the inner wall of the chamber 2 by a centrifugal force. Next, when the mixed powder 5 passes through the gap between the inner 3 and the inner wall of the chamber 2, the resin powder 10 and the alumina powders 11 are pressed against each other by a shear force, and part of the alumina powders 11 are embedded into the surface of the resin powder 10. Then,

the mixed powder 5 passed through the inner 3 is scraped off by the scraper 4, and a similar process is repeated. Finally, as shown in Figure 1, part of the alumina powders 11 are embedded so that the entire surface of the resin powder 10 is covered. At that time, the amount of alumina powders 11 being embedded into the resin powder 10 is preferably about 50-80% of the powder volume to make the peeling-off prevention at a time of high-temperature drying or baking more reliable, and the gap between the inner wall of the chamber 2 and the inner 3 is appropriately adjusted. [0012] Also, the chamber 2 may be heated during the press-contact mixture. The resin powder 10 is softened by heating, and the alumina powders 11 are easily embedded. However, since a heat is slightly generated by the pressure action of the inner 3, the press-contact mixture can be carried out at normal temperature, if shortening of time, etc., are not particularly required.

[0013] Also, the mixture ratio of the resin powder 10 and the alumina powders 11 is not particularly limited, and though it depends on each particle diameter, for example, the resin powder 10 and the alumina powders 11 may be charged at each equal amount by weight ratio.

[0014] Next, the precursor obtained is baked, so that the resin powder 10 is gasified and burnt down and the alumina

powders 11 are bound. As the baking conditions, sufficient temperature and time for completely burning down the resin powder 10 are appropriately set in accordance with the kind of resin.

[0015] In the baking process of the above-mentioned precursor, a temperature process that puts the precursor into electric furnace, etc., and gasifies and bakes it by slowly raising the temperature from room temperature may be employed, or a temperature process that puts the precursor into an electric furnace heated to a temperature for completely gasifying the resin powder 10, treats it, and raises the temperature to a temperature for binding the alumina powders 11. In particular, with the adoption of the latter temperature process, since the resin powder 1 is instantly gasified and burnt down, alumina hollow particles nearer a true sphere can be obtained. Also, the treatment temperature of the precursor in the latter temperature process is appropriately 700-800°C, though it depends on the kind of resin powder 10.

[0016] The alumina hollow particles of the present invention are obtained by the above-mentioned baking, and since the alumina powders 11 are not peeled off and dropped from the resin powder 10 during the baking, a homogenous strong porous shell layer is formed.

[0017] Also, in the present invention, there is no limitation in the kind of resin powder 10, however a soft resin is preferable so that the alumina powders 11 are embedded into it. For example, powders composed of polystyrene, polymethyl methacrylate, polyethylene, and polypropylene can be appropriately used. Among them, as shown in the results of a differential thermal analysis by Figure 3, the polymethyl methacrylate (PMMA) is preferable since it is rapidly decomposed at lower temperature, compared with the polystyrene (PS) and the polyethylene (PE), and residues are appropriately completely removed at about 350°C. With the use of this polymethyl methacrylate powder, as also will be shown later in application examples, alumina hollow particles nearer a true sphere can be obtained.

[0018] Also, the particle diameter of the resin powder 10 is appropriately selected in accordance with the particle diameter of intended alumina hollow particles. In the present invention, the generation of alumina hollow particles with a particle diameter of 20  $\mu\text{m}$  or smaller is one of the purposes, and at that time, the resin powder 10 classified to a particle diameter of 20  $\mu\text{m}$  or smaller is used.

[0019] Furthermore, the alumina powders 11 and silica powders with a diameter smaller than that of the alumina powders 11 are preferably mixed and subjected to the press-contact mixture with the above-mentioned resin powder 10. Thus, during the press-contact mixture with the resin powder 10, the silica powders with a small diameter are introduced into the gaps of the alumina powders 10 with a large diameter, so that a denser porous shell layer can be formed. Also, the amount of silica powder is less than 50 wt% of the mixture of the alumina powders 11 and the silica powders and is preferably set in a range of 3-20 wt% in terms of strength of the alumina hollow particles being generated.

[0020]

(Application examples)

Next, the present invention is further explained by application examples, however the present invention is not limited at all to them.

[0021] Application Example 1

In a mechanofusion system (AM-15F made by Hosokawa Micron K.K.; see Figure 2), polymethyl methacrylate powder classified to an average particle diameter of 20  $\mu\text{m}$ , alumina powders classified to an average particle diameter of 0.2  $\mu\text{m}$ , and silica powders classified to an average

particle diameter of 0.11  $\mu\text{m}$  were charged at a mixture ratio shown in Table 1, and its chamber was rotated at 2,500 rpm for 30 min, so that a precursor was obtained. Also, the gap between the inner and the chamber was set to 1 mm.

[0022]

(Table 1)

/4

Table 1

	配合比 (重量%)		
	アルミナ粉末のみ	シリカ粉末 5%配合	シリカ粉末 10%配合
ポリメチルメタクリレート粉末	50.0	48.7	47.8
アルミナ粉末	50.0	48.7	47.8
シリカ粉末	0.0	2.6	5.0

1. Mixture ratio (wt%)
2. Only alumina powders
3. Mixture of 5% silica powders
4. Mixture of 10% silica powders
5. Polymethyl methacrylate powder
6. Alumina powders
7. Silica powders

[0023] Then, the precursor obtained was put into an electric furnace, and the polymethyl methacrylate was first gasified by heating in a temperature range of 250-400°C at a temperature rise rate of 0.1°C/min in the air. Then, after the temperature was raised to 400-1,600°C at a temperature rise rate of about 5°C/min, the precursor was held and baked at 1,600°C for 3 h and cooled down to room temperature at a temperature drop rate of 5°C/min.

[0024] The state right after drawing the reaction product out of the electric furnace was photographed, and the electron micrograph obtained is shown in Figure 4. (a) of the figure shows the case where only the alumina powders were used, (b) shows the case where the silica powders were mixed at 5 wt%, and (c) shows the case where the silica powders were mixed at 10 wt%. (b) and (c) in which the silica powders were mixed, the alumina hollow particles favorably maintain a spherical shape, and the coagulation of the alumina hollow particles is also reduced.

[0025] Also, Figure 5(a) shows an electron micrograph in which the surface of the alumina hollow particles at a mixture of 5 wt% silica powders is photographed, and Figure 5(b) shows an electron micrograph in which its cross section is photographed. It is understood that these alumina hollow particles are hollow bodies that have a

nearly complete spherical shape and are composed of a thick homogenous porous shell layer.

[0026] Also, the particle diameter of each alumina hollow particle obtained was measured, and its cumulative particle size distribution was attained. The results are shown in Figure 6. For comparison, the cumulative particle size distribution of the polymethyl methacrylate powder used was also described. Any of the cumulative particle size distributions of each alumina hollow particle adopts a shape in which the cumulative particle size distribution of the polymethyl methacrylate is moved parallel to the large-diameter side. From this fact, it is understood that the particle diameter of the alumina hollow particles generated can be controlled, compared with the particle diameter of the resin powder used. Furthermore, with the mixture of the silica powders, it is understood that the particles with a large diameter are reduced and alumina hollow particles with a uniform particle diameter can be obtained.

#### [0027] Application Example 2

In the mechanofusion system (AM-15F made by Hosokawa Micron K.K.; see Figure 2), a polymethyl methacrylate powder classified to an average particle diameter of 10  $\mu\text{m}$  and a mixture (5 wt% silica powders) of alumina powders classified to an average particle diameter of 0.2  $\mu\text{m}$  and



silica powders classified to an average particle diameter of 0.11  $\mu\text{m}$  were charged, and its chamber was rotated at 1,000 rpm for 30 min, so that a precursor was obtained. Also, the gap between the inner and the chamber was set to 1 mm.

[0028] First, the precursor obtained was put into an electric furnace heated to 700°C, and the polymethyl methacrylate was instantly gasified. Then, after the temperature was raised to 1,600°C at a temperature rise rate of about 5°C/min, the precursor was held and baked at 1,600°C for 3 h and cooled down to room temperature at a temperature drop rate of 5°C/min.

[0029] The state right after drawing the reaction product out of the electric furnace was photographed, and the electron micrograph obtained is shown in Figure 7. (a) of the figure shows the surface, and (b) shows the cross section. It is understood that these alumina hollow particles are hollow bodies that are nearer a true spherical shape, compared with the alumina hollow particles (see Figure 5) of Application Example 1, and are composed of a thick homogeneous porous shell layer.

[0030]

(Effects of the invention)

As explained above, according to the present invention, ceramic hollow particles in which the binding force of the alumina powders is strong, a homogeneous strong porous shell layer is formed, and the shape is near a true sphere can be manufactured. Also, the manufacturing method of the present invention is suitable for the manufacture of fine alumina hollow particles with a particle diameter of 20  $\mu\text{m}$  or smaller in which the increase of its demand will be anticipated in the future.

#### 4. Brief description of the figures

Figure 1 explains the method for manufacturing alumina hollow particles of the present invention and schematically shows a precursor composed of a resin powder and alumina powders.

Figure 2 is a schematic diagram for explaining the constitution of a manufacturing apparatus being suitably used for the method for manufacturing alumina hollow particles of the present invention.

Figure 3 shows the differential thermal analysis results of a resin powder usable in the present invention.

Figure 4 is an electron micrograph in which the state right after sintering the alumina hollow particles obtained in Application Example 1. (a) shows the case where only the alumina powders were used, (b) shows the case where silica powders were mixed at 5 wt%, and (c) shows the case where silica powders were mixed at 10 wt%.

Figure 5 is an electron micrograph in which the surface (a) and the cross section (b) of a single element of the alumina hollow particles (5 wt% silica powders mixed) obtained in Application Example 1 is photographed.

Figure 6 is a graph showing a cumulative particle size distribution of each alumina hollow particle obtained in Application Example 1.

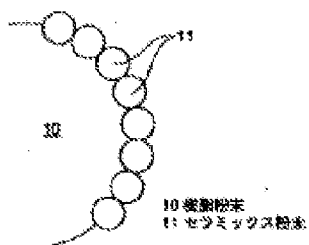
Figure 7 is an electron micrograph in which the surface (a) and the cross section (b) of a single element of the alumina hollow particles (5 wt% silica powders mixed) obtained in Application Example 2 is photographed.

Figure 8 explains a conventional method for manufacturing alumina hollow particles and schematically shows a precursor composed of a resin powder and alumina powders.

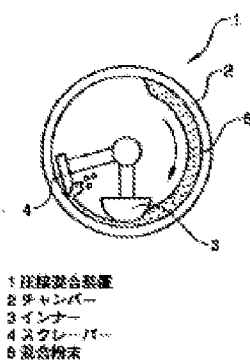
Explanation of symbols:

- 1 Press-contact mixer
- 2 Chamber
- 3 Inner
- 4 Scraper
- 5 Mixed powder
- 10 Resin powder
- 11 Alumina powder

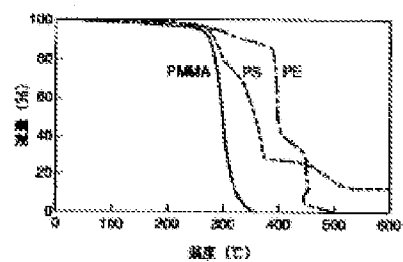
【図1】



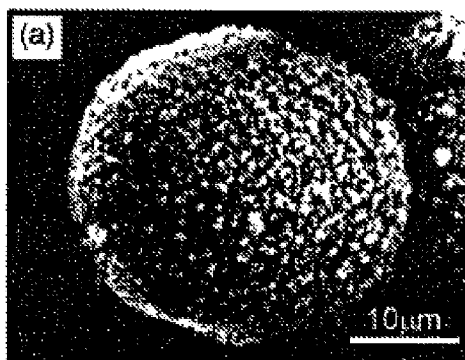
【図2】



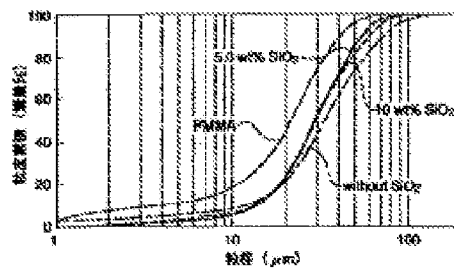
【図3】



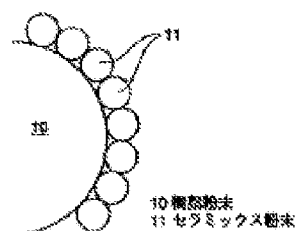
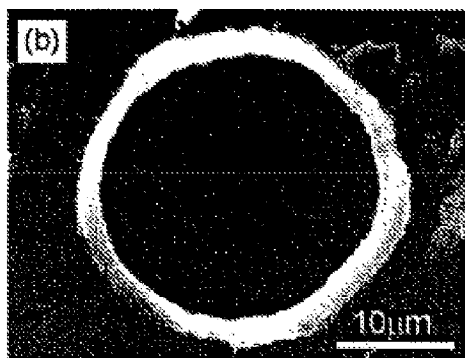
【図5】



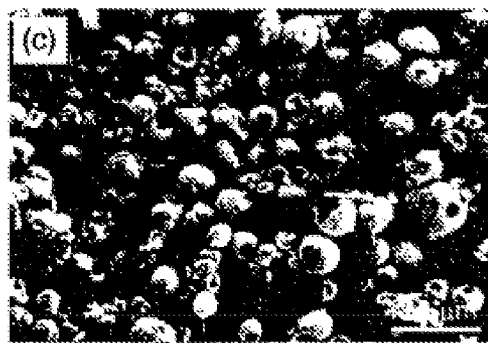
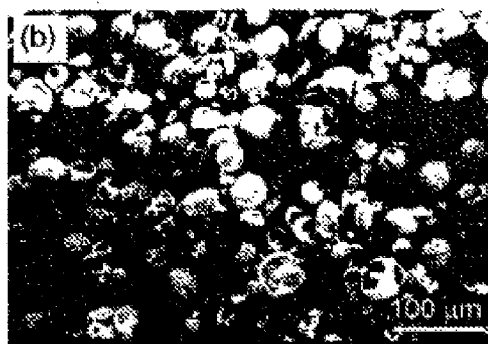
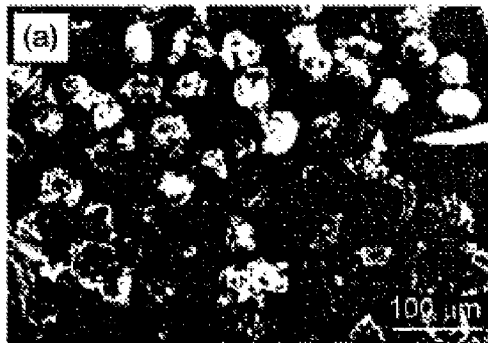
【図6】



【図8】



【図4】



【図7】

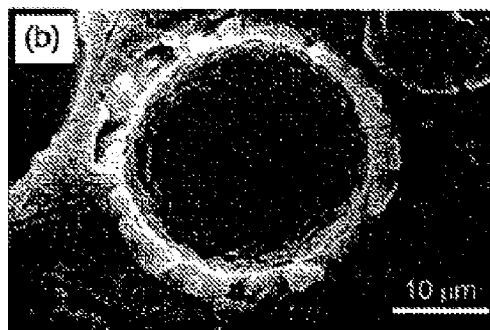
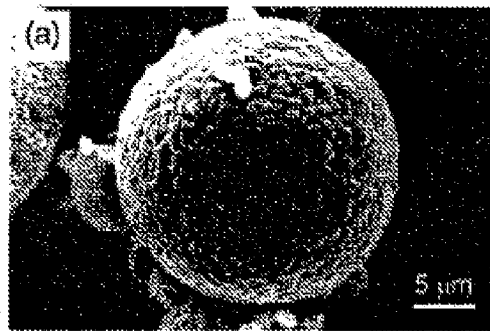


Figure 1:

- 10 Resin powder
- 11 Alumina powder

Figure 2:

- 1 Press-contact mixer
- 2 Chamber
- 3 Inner
- 4 Scraper
- 5 Mixed powder

Figure 3:

1. Amount reduced (%)
2. Temperature ( $^{\circ}\text{C}$ )

Figure 6:

1. Cumulative particle size (wt%)
2. Particle size ( $\mu\text{m}$ )

Figure 8:

- 10 Resin powder
- 11 Alumina powder